

Supporting Information for

Giant Barocaloric Effects in Natural Rubber: A Relevant Step toward Solid-State Cooling

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Materials and Methods

Samples

The natural rubber (NR) samples were prepared from a pre-vulcanized latex resin (from Siquiplas), cast into a cylindrical plaster mold. A resin feeder was used to prevent the formation of cavities due to the shrinkage of the latex while drying. We made two samples with the following dimensions: 12 mm (diameter) and 19.5 mm (length); 8 mm (diameter) and 21.1 mm (length). The density of the samples is $902(7) \text{ kg m}^{-3}$. For pressures $\leq 173 \text{ MPa}$, we used the 12 mm-diameter sample; above 173 MPa, the 8-mm-diameter sample was used. We characterized the 12-mm-diameter sample via Fourier transform infrared spectroscopy (FTIR) from 450 to 4000 cm^{-1} , with a fixed step of 2 cm^{-1} , using a FTIR spectrometer from PerkinElmer® (model Spectrum Two). The absorption bands observed in the spectrum (Fig. S1) are typical of NR samples.

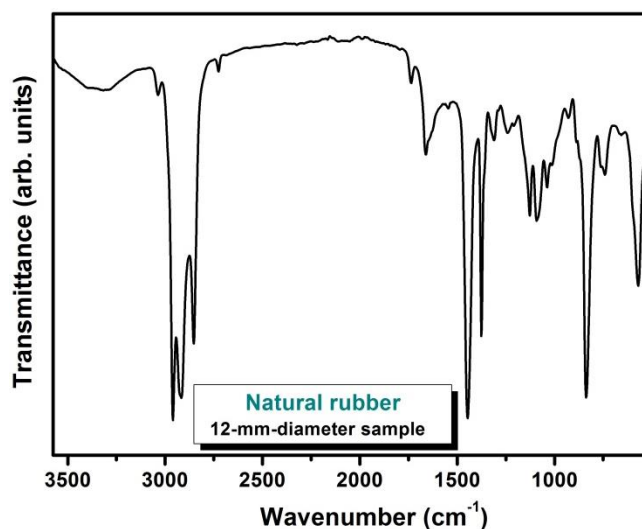


Figure S1. FTIR spectrum of the 12-mm-diameter sample of natural rubber.

Experimental setup

The experimental setup consists of a customized piston-cylinder carbon-steel chamber surrounded by a copper coil, enabling the circulation of cooling/heating fluids (water or liquid nitrogen, for instance). Two tubular heating elements (NP 38899, HG

Resistências), placed in the proper holes in the chamber, are responsible for thermal stability when liquid nitrogen is used. Temperature is measured by two type-K thermocouples. A thermostatic bath (TE 184, Tecnal) was used to pump water in the copper coil above 280 K. Below 280 K, liquid nitrogen was employed to cool down the sample. Uniaxial load is applied by a manual 15,000-kgf hydraulic press (P15500, Bonevau). A load cell (3101C, ALFA Instrumentos) measures the contact force. Sample displacement is probed by a precise linear length gauge (METRO 2500, Heidenhain Co). Temperatures are collected and controlled (if heating elements are used) by Cryogenic Temperature Controller (Model 335, Lake Shore Cryotronic). This system is described in details by Bom et al (ref. 31, main text).

Description of the barocaloric experiments

The direct measurements of barocaloric temperature changes (ΔT_s) were obtained by the following procedure: i) the sample was submitted to compressive stresses quasi-adiabatically, resulting in an immediate increase in temperature; ii) the load was kept constant, until the temperature decreases down to the initial temperature; iii) the load was released adiabatically, causing an abrupt decrease in the sample's temperature. ΔT_s curves for 273 and 390 MPa were measured from the maximum temperature (~ 314 K) down to minimum temperature (~ 223 K). Before starting the actual measurements, we have always performed several cycles in the maximum pressure until stabilizing the ΔT_s value. The experiments were carried out only when the temperature in the sample was stable. Strains vs. temperature curves for NR (Fig. S2), used in the calculation of entropy variations shown in Fig. 3 (main text), were measured at different constant pressures (8.7 – 173 MPa). Temperature was varied continuously by the thermostatic bath within the temperature range of $\sim 285 - 330$ K.

Glass-transition temperature vs. pressure data

The glass-transition temperatures (T_g) for NR at different pressures were measured by differential scanning calorimetry (DSC) and strain (ϵ) vs. temperature (T) curves. DSC measurement was carried out under atmospheric pressure, with heating rate of 10 K/min, from 186 K to 416 K. ϵ vs. T curves for obtaining T_g were measured in an analogous

manner of ϵ vs. T curves for ΔS_T , but within a temperature range of 173–303 K; here, the T_g values were obtained during heating process, when $d^3\epsilon/dT^3 = 0$.

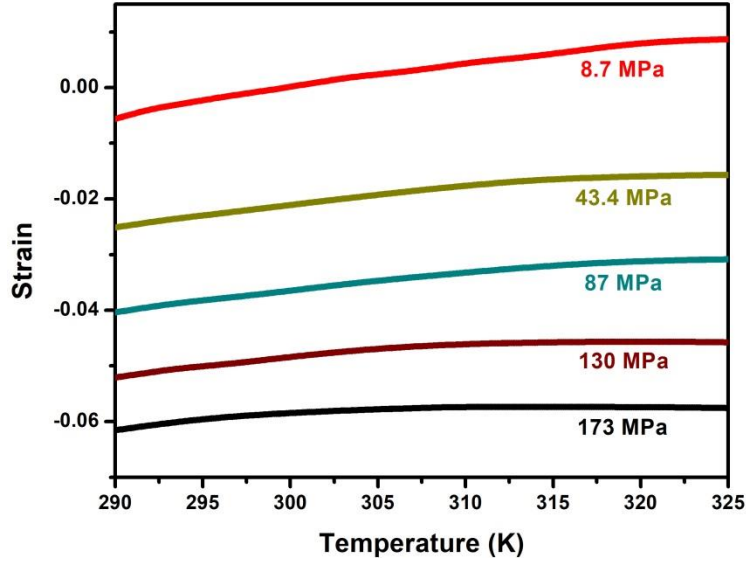


Figure S2. Strain vs. temperature curves for natural rubber at constant pressures of 8.7(2), 43.4(9), 87(2), 130(3) and 173(3) MPa measured on cooling, which were used to calculate the isothermal entropy change shown in Fig. 3 (main text).

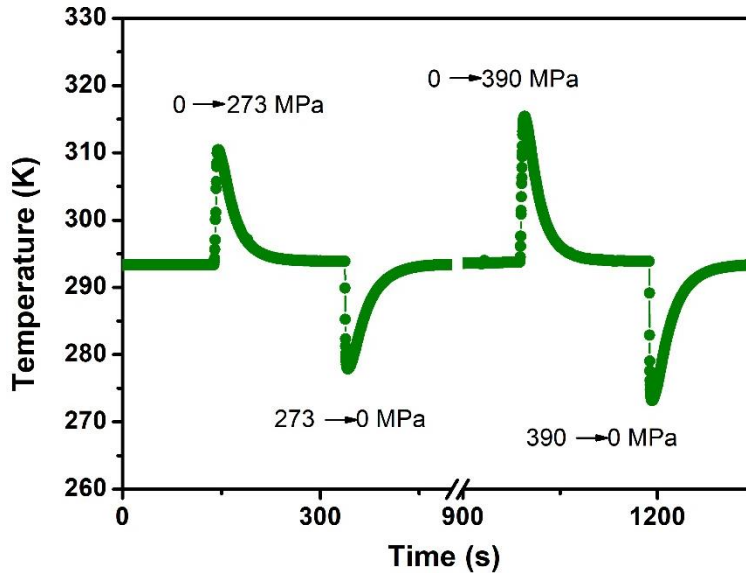


Figure S3. Temperature vs. time for NR at initial temperature of ~293 K; the peaks (or the valleys) are related to the adiabatic temperature change (ΔT_s) when the pressures of 273(8) and 390(12) MPa are applied (or released).

Table S1. Fitting parameters of $-\Delta T_S$ vs. $\sigma_{\max}$ curves for NR, obtained from the power law $-\Delta T(T, \sigma_{\max}) = a_T \sigma_{\max}^{n_T}$ (equation (2), main text).

Temperature (K)	a_T (K GPa $^{-n_T}$)	n_T
273	54(3)	0.96(4)
293	61(5)	0.98(6)
313	63(4)	0.96(5)

Table S2. Fitting parameters of $-\Delta S_T$ vs. $\sigma_{\max}$ curves for NR (Fig. 4b), obtained from the power law $-\Delta S(S, \sigma_{\max}) = a_S \sigma_{\max}^{n_S}$ (equation (2), main text) and from the quadratic function $\Delta S(T, \sigma) = a_1(T)\sigma + a_2(T)\sigma^2$ (equation (4), main text).

Temperature (K)	a_S (K GPa $^{-n_S}$)	n_S	a_1 (kJ kg $^{-1}$ K $^{-1}$ GPa $^{-1}$)	a_2 (kJ kg $^{-1}$ K $^{-1}$ GPa $^{-2}$)
295	0.74(4)	1.16(2)	0.42(2)	0.8(1)
300	0.67(5)	1.16(3)	0.37(2)	0.8(2)
305	0.48(8)	1.09(7)	0.37(2)	0.3(3)

Appendix A: Derivation of the expression for $\Delta S(T, \sigma)$ from a modified Landau's theory of elasticity

Let us regard the Helmholtz free energy per unit volume as the following series expansion:¹

$$F(T, \varepsilon_{ij}) = F_0(T) - B\alpha(T - T_0)\varepsilon_{kk} - \frac{1}{2}B[\beta(T - T_0)^2 - 1]\varepsilon_{kk}^2 + G\left(\varepsilon_{ij} - \frac{1}{3}\varepsilon_{kk}\delta_{ij}\right)^2$$

where F_0 is the free energy of the unstrained samples, α is the thermal expansion coefficient; β accounts for a non-linear thermal deformation of the sample; B and G are the bulk and shear moduli, respectively; δ_{ij} is the unit tensor. The notation above implies summation over repeated indexes (which can be x , y or z in Cartesian coordinates). Furthermore, T_0 is a reference temperature where the sample experiences no thermal

deformation. The expansion above converts the components of a rank-two tensor (the strain tensor ε_{ij}) into a scalar.

It is possible to obtain the entropy through the derivative of the free energy with respect to temperature:

$$S = -\frac{\partial F}{\partial T} = S_0 + B\alpha\varepsilon_{kk} + B\beta(T - T_0)\varepsilon_{kk}^2 \quad (1)$$

On the other hand, the internal stress is obtained differentiating the free energy with respect to the strain:

$$\sigma_{ij} = \frac{\partial F}{\partial \varepsilon_{ij}} = -B\alpha(T - T_0)\delta_{ij} - B\beta(T - T_0)^2\varepsilon_{kk}\delta_{ij} + B\varepsilon_{kk}\delta_{ij} + 2G\left(\varepsilon_{ij} - \frac{1}{3}\varepsilon_{kk}\delta_{ij}\right) \quad (2)$$

Let us now consider the case of confined compression by a uniaxial stress, and let us assume that the stress is applied along the z axis. Therefore, the only non-vanishing component of the strain tensor is ε_{zz} . From equation (2), the component σ_{zz} is:

$$\sigma_{zz} = -B\alpha(T - T_0) + \left\{B[1 - \beta(T - T_0)^2] + \frac{4}{3}G\right\}\varepsilon_{zz} \quad (3)$$

Finally, combining equations (1) and (3), the entropy change can be expressed as a second-degree polynomial of the applied compressive stress:

$$\Delta S(T, \sigma) = a_1(T)\sigma + a_2(T)\sigma^2$$

Appendix B: Satisfying the isostatic condition

The zz -component of the stress tensor above is related to the external applied stress $\sigma_{zz} = -\sigma$ (negative because the stress is compressive). The other diagonal components are:

$$\sigma_{xx} = \sigma_{yy} = -B\alpha(T - T_0) + \left\{B[1 - \beta(T - T_0)^2] - \frac{2}{3}G\right\}\varepsilon_{zz}$$

which are the components of the stress applied by the walls confining the sample and are responsible for keeping $\varepsilon_{xx} = \varepsilon_{yy} = 0$. If one considers, for the sake of simplicity, the temperature $T = T_0$, then the ratio σ_{xx}/σ_{zz} becomes:

$$\frac{\sigma_{xx}}{\sigma_{zz}} = \frac{3B - 2G}{3B + 4G}$$

For natural rubber, $B = 2 \times 10^9$ Pa and $G = 3.33 \times 10^4$ Pa,² which results in $\sigma_{xx}/\sigma_{zz} = 0.999967$. Therefore, uniaxial compression of natural rubber is actually an isostatic compression.

References

1. Landau, L. D.; Lifshitz, E. M., In *Theory of Elasticity: Vol. 7 of Course of Theoretical Physics*, 2nd ed.; Pergamon Press: Oxford, 1970.
2. Tabor, D. *Polymer*. **1994**, 35, 2759– 2763.